

THE THERMAL CRACKING OF COAL-DERIVED MATERIALS

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SUMMARY

Up to 27% benzene, toluene and xylenes and 24% ethylene were obtained by cracking a highly hydrogenated coal extract, compared to less than 4% of each from unhydrogenated coal, coal extract and anthracene oil. The importance of naphthenes as BTX and ethylene precursors was confirmed.

INTRODUCTION

Many of the feedstocks for the chemical industry, especially aromatic hydrocarbons, were originally obtained as byproducts from the carbonisation of coal (1,2). However, nowadays most of these chemical feedstocks are derived from petroleum. Nevertheless, it is probable that, within the next few decades, the shortage of world reserves of petroleum will mean that BTX will once again have to be produced from coal, as will ethylene. It is, therefore, appropriate to examine ways in which these materials can be produced from coal; the present investigation was designed to study the formation of BTX and ethylene by the thermal cracking of coal-derived materials from the NCB coal liquefaction/hydrogenation processes (3).

EXPERIMENTAL

Feedstocks

The vapours from the carbonisation of a bituminous, low-rank coal, an anthracene oil and a coal extract in anthracene oil were diluted with nitrogen and cracked; their product yields were compared with those from the cracking of a partially hydrogenated anthracene oil and coal extracts hydrogenated to various extents. The coal was Linby (National Coal Board, Coal Rank Code 802) and the extract was prepared by digestion at 673 K and 8 bar in anthracene oil, filtration to remove mineral matter and dissolved coal, followed by distillation under reduced pressure until the extract contained about 70% coal. The two coal extract hydrogenates were prepared by catalytically reducing a dilute extract from Annesley (NCB, CRC 702) coal in a trickle bed reactor and fractionating the product. The fractions were further reduced in a vapour phase reactor to give two highly hydrogenated liquids.

Four model compounds, n-undecane, tetralin, cis/trans decalin and mesitylene, and a natural gas condensate from the North Sea were also cracked. Analyses and the reference code key of the coal-based feedstocks and the gas condensate are given in Table 1. Paraffin, naphthene and aromatic type analyses were calculated from gas chromatographic analyses of the partially hydrogenated anthracene oil and gas condensate, whereas mass spectrometric analysis was performed on the two coal extract hydrogenates and their further hydrogenated products.

Apparatus and Procedure

The experiments with the solid feedstocks and the initial experiments on liquid samples were carried out in the apparatus shown in Figure 1a. The vapours from a stainless steel, stirred-bed carboniser/vaporiser at 873 K were cracked at atmospheric pressure in a tube reactor heated in a platinum-wound furnace.

The reactor was 30 mm ID and had a 100 mm long hot zone within 20 K of the maximum reactor temperature. Solid feedstocks were introduced at about 1 g min⁻¹ from a vibratory table through a water-cooled port. Liquids were injected at the same point from a mechanically driven syringe at 0.1 to 0.8 ml min⁻¹. The amount fed was determined by weighing the feeders.

Liquid products were collected in two glass traps at 258 K and in a glass wool filter. The gas was measured in a dry gas meter and sampled over mercury into glass bottles. The reactor and collection train were weighed and the liquids removed with a known amount of chloroform. The effects of vapour residence time and cracking temperature on the product yields from each feedstock were investigated. The effects of variables such as reactor surface, type and area, feedstock vapour concentration and the addition of steam was also tested over a limited range of conditions with a hydrogenated coal extract. Gaseous and liquid products were analysed by chromatography.

Later experiments with the hydrogenated feedstocks, which were completely vaporisable, were performed by injecting the liquids into the top of the smaller reactor (9 mm ID) shown in Figure 1b: the liquid feed rate was only a tenth of that required for the larger apparatus; the furnace and collection systems were similar. Comparative tests with cis/trans decalin and hydrogenated anthracene oil showed that the smaller reactor gave marginally higher BTX and ethylene yields than the larger reactor.

RESULTS

The Effect of Surface, Reactant Concentration and Diluent

Results from the cracking of a hydrogenated coal extract similar to (D) in the larger reactor with and without copper or stainless steel packing, which increased the surface area about threefold whilst decreasing the reactor volume by only 10%, showed that neither copper nor stainless steel significantly affected the yields of BTX and ethylene. An eightfold reduction in the concentration of the feedstock vapour (at constant vapour residence time) also had no significant effect. Replacement of part of the diluent nitrogen to give a 70% steam + 30% nitrogen mixture had a negligible effect on the yields of BTX and ethylene although xylenes were favoured at the expense of benzene.

Unhydrogenated Coal-derived Materials

Preliminary experiments on cracking the vapour from coal extract (B) at 1133 K for 0.7 to 8 s showed that the BTX yield peaked at 2 s whereas ethylene was favoured by shorter residence times. Figure 2 shows the effect of cracking temperature at 2 s vapour residence time on the yields of BTX, benzene and ethylene from Linby coal (A), coal extract (B) and anthracene oil (C). Yields of BTX and benzene peaked at about 1273 K whereas the maximum ethylene yields were obtained at about 1100 K. The mass balances and yields of the gaseous and liquid products at one condition, 1273 K for 2 s, are given in Table 2.

The yields of BTX and ethylene are low, less than 3.5% BTX and 1.5% ethylene: the highest yields were from Linby coal. Although the BTX yields are greater than the 1% from conventional, high temperature coal carbonisation (2), they are only a fraction of those obtainable from petroleum feedstocks (4).

Hydrogenated Coal-derived Materials

The yields from the partially hydrogenated anthracene oil (C1), two coal extract hydrogenates (D and E) and their further hydrogenated products (D1 and E1) when cracked at 1133 K, which favoured ethylene formation, are listed in Table 2 together with the yields from the gas condensate at 1158 K. The BTX,

benzene and ethylene yields from the two further hydrogenated materials (D1 and E1) are plotted against cracking temperature in Figure 3.

Table 2 shows that the parent hydrogenates (D and E) gave relatively low yields of BTX and ethylene (<10%) whereas considerable yields of polynuclear aromatics such as naphthalene, methyl naphthalenes, acenaphthylene, fluorene, anthracene and phenanthrene were obtained. In contrast, the further hydrogenated materials (D1 and E1) gave higher yields of BTX and ethylene (>20%) and relatively low yields of polynuclear aromatics. The highest yields of BTX, 27% at 1083 K for 1 s and at 1108 K for 0.4 s, and of ethylene, 24% at 1158 K for 0.4 s, were both obtained from D1. The curves in Figure 3 for a vapour residence time of 0.4 s show broad maxima in BTX and ethylene yields; similar maxima were obtained at 1 and 2 s but at slightly lower cracking temperatures.

The yields from the partially hydrogenated anthracene oil (C1), also given in Table 2, are relatively low, little more than 10% BTX and ethylene being obtained.

Natural Gas Condensate

To compare the yields from coal-derived materials with those from a petroleum material, a full range, North Sea gas condensate (F) was cracked at 1158 K for 0.4 s. Its analysis is given in Table 1 and the yields obtained are listed in Table 2. More ethylene (30%) but less BTX (16%) were produced than from the highly hydrogenated coal materials.

Model Compounds

Four model compounds (mesitylene for aromatics, tetralin for hydroaromatics, decalin for naphthenes and n-undecane for paraffins) were cracked singly and as mixtures at 1133 K for 1 s. The yields of BTX, ethylene, butadiene and methane are shown as a bar chart in Figure 4. Decalin gave the highest BTX yield, 25%, compared with less than 7% from n-undecane. Mesitylene gave only 8% BTX. Tetralin produced the least BTX, 3%, its major products being polynuclear aromatics. n-Undecane gave 37% ethylene compared to 20% from decalin, 3% from tetralin and 0.2% from mesitylene. Six binary, four ternary and the quaternary mixtures of the four compounds were cracked and the observed product yields were within $\pm 2\%$ of the values calculated from the constituents' yields.

DISCUSSION

The low yields of BTX and ethylene from the unhydrogenated feedstocks reflect the stability of the condensed aromatic structures which constitute much of their volatiles and confirm the findings of a literature review (5). It is interesting that the coal extract (B), which contained 70% coal, yielded even less BTX and ethylene than the coal itself; this is probably due to elimination of reactive constituents and cross-linking during digestion/extraction of the coal.

Yields of BTX and ethylene increased with increasing extent of hydrogenation of coal extract, as indicated by the H/C ratios listed in Table 1. This was reflected in their naphthene contents, which were in the order D1 > E1 > D > E, and confirms the finding (6) that polynuclear aromatic hydrocarbons need to be fully hydrogenated to the naphthenic structure to maximise their conversion to BTX and ethylene. Concomitantly, the yields of tar and polynuclear aromatics decreased with decrease in the (hydroaromatic + aromatic) content of the feedstock, suggesting that the higher aromatics result from the dehydrogenation of hydroaromatics to the parent aromatics and from the survival of those aromatic hydrocarbons already present. 34% of C₂-C₄

gaseous hydrocarbons (C_2H_6 , C_2H_4 , C_3-C_4 unsaturates and saturates) were obtained from E1 at 1133 K for 0.4 s (up to 17% C_3-C_4 unsaturates were obtained at a lower cracking temperature of 1083 K). The sum of BTX + valuable gaseous hydrocarbons amounted to 55% at 1133 K, 60% at lower temperatures.

Some acetylene and polyacetylenes, which are undesirable, explosive byproducts, were also formed. The amount increased with the severity of cracking but was only 2.5% of the maximum ethylene yield; this value is about that found in the industrial cracking of petroleum naphtha to ethylene (7,8).

Cracking temperature and vapour residence time were the most important parameters controlling the cracking reactions. Within the range of conditions tested, other variables such as type and area of cracking surface, the vapour concentration of the feedstock and presence of steam made little difference to the yields of BTX and ethylene. Steam is used as a diluent and carrier in industrial ethylene crackers, where it reduces carbon laydown in the reactors (9).

The aromatic and hydroaromatic components of coal-derived feedstocks are potential sources of carbon laydown and steam would be needed to reduce reactor fouling.

The high ethylene and moderate BTX yields from the gas condensate are commensurate with its 56% paraffin and 12% naphthene content (see Table 1). This was confirmed by the 37% ethylene and 7% BTX obtained from the model paraffin, n-undecane (see Figure 4).

The model compound studies confirmed that the molecular structure of the hydrogenated coal extract is of paramount importance in determining the product pattern: hydroaromatics dehydrogenate to aromatics, which either survive or polymerise to tars and, eventually, to carbon; naphthenes crack principally to BTX and ethylene; aliphatics mainly give small unsaturates such as ethylene and butadiene. The abnormally low yield of BTX from mesitylene is attributed to its high symmetry and thermal stability.

CONCLUSIONS

The results from the thermal cracking of unhydrogenated and hydrogenated coal-derived materials, a gas condensate and model compounds led to the conclusions that:

- (i) only low (< 3.5%) BTX and ethylene yields were obtained by cracking the vapours from a bituminous coal, an anthracene oil and the anthracene oil extract of the coal;
- (ii) the BTX and ethylene yields increased with increasing extent of hydrogenation of the extract (which increased the naphthene content); tar was mainly derived from the aromatic and hydro-aromatic components;
- (iii) about 27% BTX and 24% ethylene were obtained from the highly hydrogenated coal extract; in comparison, a paraffinic North Sea gas condensate gave 16% BTX and 30% ethylene;
- (iv) the product yields from mixtures of model compounds were predicted to within $\pm 2\%$ from those of the constituents.

ACKNOWLEDGEMENTS

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Table 1 Analysis of Feedstocks

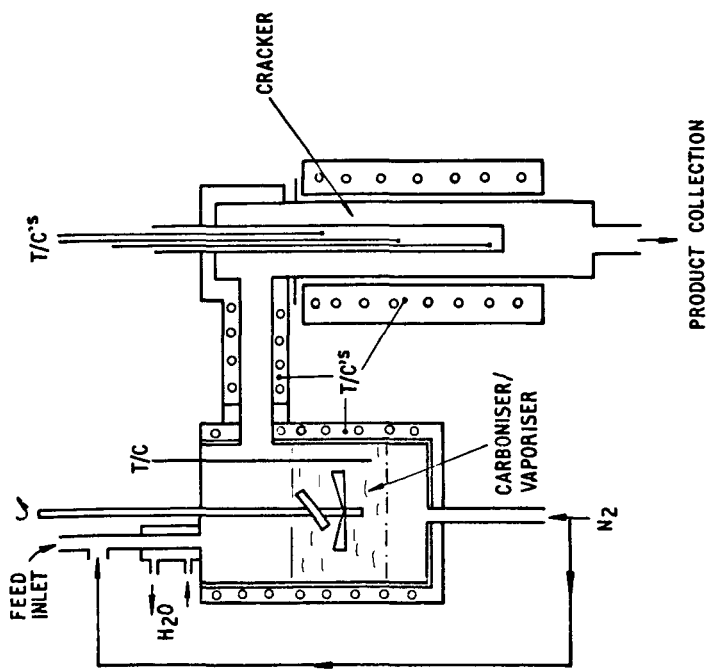
Solid Feedstock	Key	Size, μ m	Proximate Analysis, % w/w			Ultimate Analysis, % w/w d.a.f.						H/C atomic ratio
			Moisture, a.d.	Ash, a.d.	V.M. d.a.f.	C	H	O	N	S		
Lumpy coal	A	210 to 350	8.3	6.0	39.1	82.4	5.3	9.0	1.95	1.00	0.77	
Anthracene oil extract of lumpy coal	B	210 to 350	0.3	0.3	50.5	88.7	4.8	3.8	1.90	0.55	0.65	
Liquid Feedstocks	Distillation range, $^{\circ}$ C	Hydrocarbon Analysis, % w/w										
		Paraffins	Aromatic hydrocarbons	Aromatics + Hydrocarbons	Unidentified							
Anthracene oil	C	573 to 673	N.D.	N.D.	N.D.	90.6	6.9	1.9	0.6	0.55	0.91	
Partially hydrogenated anthracene oil	C1	449 to 505	1.7	20.7	64.4	88.2	10.7	0.5	0.4	<0.1	1.46	
Hydrogenated coal extracts	B	443 to 523	0	28.5	71.5	0	69.4	10.1	0.7	0.25	1.36	
	E	523 to 573	0	23.7	76.2	0.1	89.6	9.4	N.D.	N.D.	1.26	
Further hydrogenated coal extracts	U1	443 to 570	0	95.5	2.2	2.3	86.4	13.2	0.5	<0.1	1.83	
	E1	473 to 573	0	90.7	6.9	2.4	86.9	13.0	N.D.	N.D.	1.78	
Natural gas condensate	F	449 to 625	56.0	11.9	14.0	18.1	85.1	14.4	<0.2	<0.1	2.03	

N.D. = Not Determined

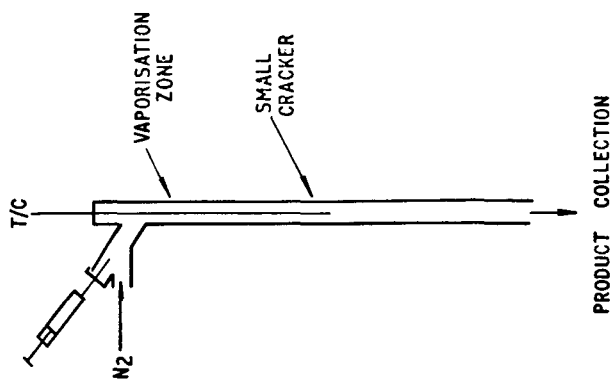
Table 2 Yields from Cracking Coal-derived Feedstocks and a Natural Gas Condensate

g w/w									
Yield	1273			1133			1156		
	2.0			1.0			0.4		
Cracking Temperature, °K									
Vapour Residence Time, s									
Feedstock	Anthracene oil extract of lumpy coal*			Partially hydrogenated anthracene oil			Hydrogenated coal extract		
	A	B	C	Cl	D	E	D1	E1	F
Product									
Benzene	3.1	1.8	2.1	6.6	3.5	2.6	17.1	13.5	11.9
Toluene	0.1	0	0	2.7	1.9	1.3	5.3	5.1	2.9
Xylene	0	0	0	1.3	1.7	1.1	3.0	2.8	1.7
Total HTX	3.2	1.8	2.1	10.6	7.1	4.9	25.4	21.4	16.1
Cl ₄	4.3	2.6	2.7	8.2	6.4	5.5	12.0	10.8	13.4
C ₂ H ₆	0.2	0	0	0.8	1.0	0.8	1.5	1.7	1.7
C ₂ H ₄	0.3	0.1	0.09	10.8	9.1	7.5	23.1	21.5	20.3
C ₂ H ₂	N.D.	N.D.	N.D.	0.3	0.1	0.1	0.4	0.1	0.2
C ₃ -C ₄ aro.	0.4	0.1	0	0	0.05	0.05	0.1	0.1	0.2
C ₃ -C ₄ unaro.	0	0	0	1.8	3.4	2.7	7.9	10.6	11.2
H ₂	1.3	1.0	1.3	1.2	1.1	0.9	1.3	1.2	1.0
CO	7.8	1.7	1.6	0	0	0	0	0	0
CO ₂	3.8	0.4	0.4	0	0	0	0	0	0
Indene	< 0.01	< 0.01	< 0.01	1.3	3.4	2.2	1.9	1.8	0.8
Naphthalene	0.3	0.2	1.4	19.5	23.5	15.6	4.6	5.3	2.9
Methyl naphthalenes	< 0.01	< 0.01	< 0.01	3.1	7.9	6.6	1.3	2.5	0.6
Diphenyl	0.03	0.01	< 0.01	1.1	3.3	4.1	0.4	0.3	0.3
Acenaphthylene	0.08	0.06	0.07	1.8	3.9	5.1	0.9	1.3	0.4
Fluorene	0.01	0	0.07	0.5	0.5	2.2	0.3	0.3	0.2
Anthracene and phenanthrene	0.2	0.2	1.7	1.4	0.4	6.0	0.9	0.2	0.2
Fluoranthene	0.06	0.2	0.4	0	0.3	0.2	0	0.1	0
Pyrene	0.06	0.2	0.4	0.5	0.3	0.3	0	0.4	0
Mass Balance									
Gas	21	13	8	28	24	20	58	57	70
Liquid/tar	17	15	56	46	69	82	29	31	14
Solid	61	72	23	10	10	5	11	5	11
Total	99	100	87	84	103	107	98	93	94

* Carbonation temperature 873 K.
N.D., Not Determined



1a. CARBONISER/VAPORISER/CRACKER



1b. SMALL VAPORISER/CRACKER

FIGURE 1. CRACKING APPARATUS

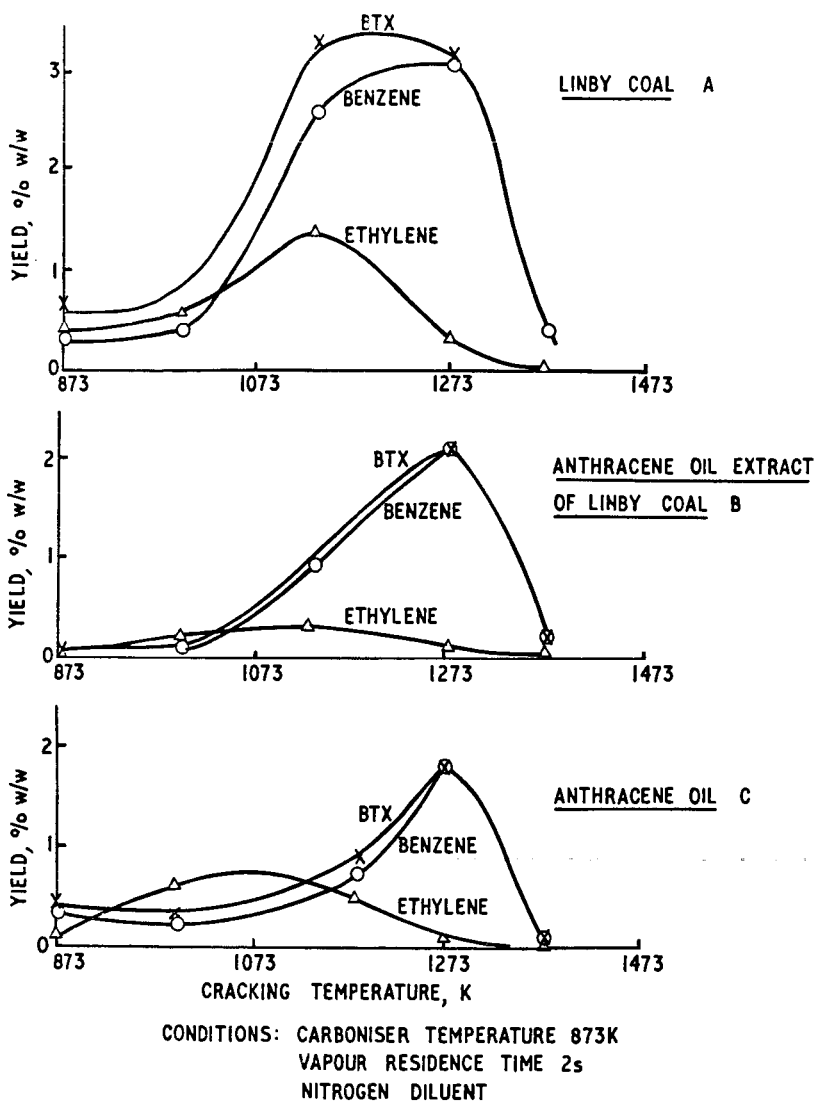
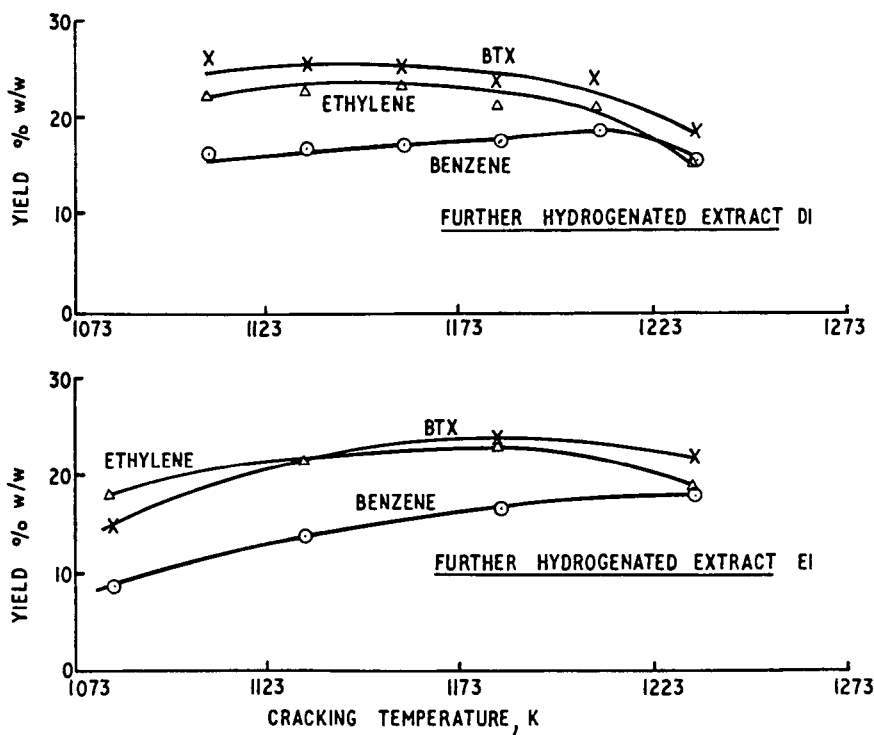
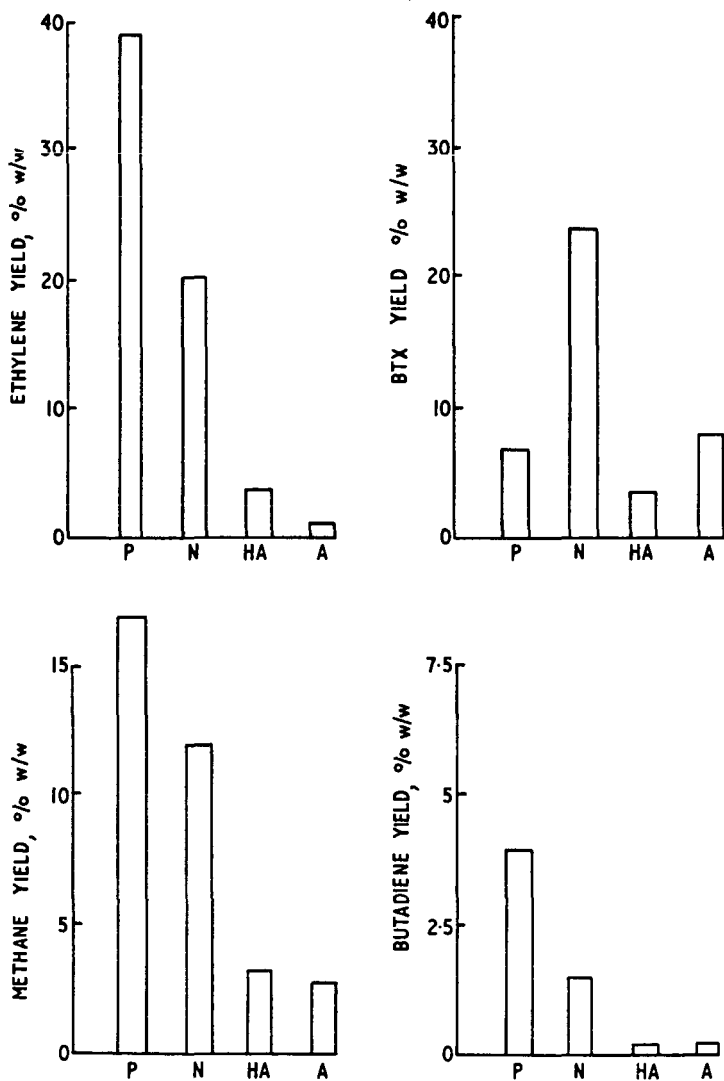


FIGURE 2. THE EFFECT OF CRACKING TEMPERATURE ON YIELDS OF BTX, BENZENE AND ETHYLENE FROM UNHYDROGENATED COAL MATERIALS.





CRACKING TEMPERATURE 1133K
VAPOUR RESIDENCE TIME 1s

KEY: PARAFFIN P=n-UNDECANE; HYDROAROMATIC HA= TETRALIN;
NAPHTHENE N= CIS/TRANS DECALIN; AROMATIC A=MESITYLENE

FIGURE 4. THE VARIATION OF YIELDS WITH HYDROCARBON TYPE